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MSM  
HISTORICAL  
COLLECTION

FURTHER STUDIES ON THE EFFECT OF GRINDING AIDS FOR  
PORTLAND CEMENT CLINKER

BY

CHARLES LEE RAKESTRAW

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A

THESIS

submitted to the faculty of the  
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI  
in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

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1947

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MSM  
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Approved by

*Frank H. Conrad*

Professor of Chemical Engineering

68003

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The able and valuable assistance along with constant encouragement given by Dr. F. H. Conrad of the Missouri School of Mines, Rolla, Missouri, is hereby gratefully acknowledged.

C. L. Rakestraw

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## FURTHER STUDIES ON THE EFFECT OF GRINDING AIDS FOR PORTLAND CEMENT CLINKER

### INTRODUCTION

In the dry grinding of cement clinker to a fine powder in which for example ninety percent or more of the particles are reduced to a fineness below that of a 200 mesh screen, it has been found that further fine grinding is extremely difficult and the energy input is out of all proportion to the further production of fine particles. This seems to be due to the fact that when the bulk of the material reaches this fineness there is a tendency of the finest particles to cling to each other and bunch or flocculate. Along with this tendency is an adhering to the balls and the sides of the mill, thus producing a cushioning effect as the balls come into contact with the material being ground. This coating adheres tightly to the balls and increases in thickness as the grinding progresses.

What is a grinding aid? A grinding aid might be thought of as a small amount of a foreign substance which is added to the material to be ground so as to facilitate the grinding operation. This is done by counteracting the tendency of the fine particles to flocculate and coat the balls and mill.

## A REVIEW OF THE LITERATURE

A search through the literature has revealed that most of the work on grinding aids was done several years ago; at least very little has been published since 1940. Of the work that has been done there are several conflicting opinions and on the whole specific methods and results are very vague.

At the present time the most promising grinding aid seems to be a patented material<sup>(1)</sup> which is manufactured by the Dewey & Almy Chemical Company, Cambridge, Massachusetts. This material, named TDA, is a mixture of triethanolamine salts and highly purified soluble calcium salts of modified lignin sulphonic acid. TDA is sold as a dry powder and is added as a 15 % aqueous solution. If the full strength of the cement is wanted, the TDA is added in a ratio of one part to 1500 parts cement; while it is added in a ratio of one part TDA to 3000 parts cement when used only as a grinding aid.

Some general conclusions<sup>(2)</sup> about TDA are: "1. TDA increases the rate of grinding of Portland cement.

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(1) Rockwood, N. C., Rock Products, Vol. 42, p. 38 (May, 1939).

(2) Dawley, E. R., Pit and Quarry, Vol. 32, p. 44, (July, 1939).

This allows an increase in the fineness of the cement. An increase in the ratio of the weight of the grinding balls to the weight of the cement causes an increase in the grinding rate, and an increase in the effect of TDA. Reducing the amount of TDA by one-half does not appreciably affect the grinding results. 2. The use of TDA produces a cement that is normal in every way. 3. The air inclusions of the TDA cement are negligible, being less than 1 per cent. 4. Cements ground in the laboratory mill with and without TDA compare very closely in particle-size distribution. 5. The laboratory and commercial-mill ground cements compare very closely in particle-size distribution. 6. TDA causes an increase in the tensile strength, particularly at 1 and 3 days. 7. When compared with the corresponding Portland cements, TDA cements produce higher compressive strength and more workable concrete, from which it follows that TDA cements make concretes with identical mix and identical workability, but with a lower water-cement ratio, or concretes with identical workability, but with more aggregate. This results either in stronger or more economical concrete. 8. Additional strength can be secured from the increase in fineness caused by the TDA in grinding the cement. 9. There is no significant difference in the density of concrete made from cement with or without TDA.

10. TDA causes an increase in the durability or resistance to freezing and thawing of the concrete."

Under present A. S. T. M. Specifications TDA is the only agent which has been accepted as "non-harmful". At the present time cement users are not being provided with the best cement for the particular job. Instead a general all purpose cement is being provided. As users gradually learn that this need not be the case, there will be a greater demand for research on grinding aids with as much emphasis being placed upon their effect upon the workability and the final concrete product as upon the rate of grinding the clinker.

Carl Pontopidan, in 1928, received a patent(3) upon a process whereby a liquid or other substance which is exposed to the action of the heat produced in the grinding mill by the grinding process and by its consequent evaporation, absorbs so much heat that the material will be cooled to below the critical temperature at which the material becomes appreciably inclined to adhere to the surfaces with which it comes into contact in the grinding machine.

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(3) Pontoppidan, Carl, British Patent 283,091, Jan. 5, 1928.

It is seen that Pontoppidan offers the theory that if the temperature in the grinding machine exceeds about 100° C., the ground material appears to become inclined to adhere to the surfaces, balls, etc. with which the material comes into contact during the grinding operation.

Apparently this theory did not prove to be very successful for in 1933 Pontoppidan offered the theory that the tendency of the fine particles to adhere to the grinding surfaces or flocculate was caused by friction between the grinding balls and the material being ground. Because of this friction a charge of static electricity was developed giving a difference in polarity between the balls or grinding surfaces and the fine particles. It is this difference in polarity or a difference of electrical potential, or both which results in the adhering of the fine particles to the grinding surfaces<sup>(4)</sup>.

To take care of this theory Pontoppidan proposed to add a carbonaceous substance to the material being ground so as to alter the electrical potential of the grinding bodies and thus diminish the attraction

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(4) Pontoppidan, Carl, United States Patent 1,904,523  
April 18, 1933.

of the fine particles to the grinding bodies. In this way the coating of the grinding bodies with the particles is prevented<sup>(5)</sup>.

Breyer held the belief that the flocculation and adherence to the grinding bodies was due to a slight film of moisture or gases which gathers on the surface of the fine particles<sup>(6)</sup>. When grinding aids are added the formation of these thin moisture films is prevented, thus there is no cohesion between the fine particles. The moisture or gas film is prevented because the grinding aid forms a very slight film upon the fine particles and upon the grinding surfaces. This film must be thin enough not to act as a flocculating agent itself. Therefore it is natural to assume that there is an optimum amount of each grinding aid for the material being ground. When more than the optimum amount has been added the efficiency either remains constant or decreases.

Since Pontoppidan<sup>(7)</sup> added water to the material being ground and Breyer<sup>(8)</sup> attributes poor grinding efficiency to a moisture film, there seems to be

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(5) Ibid.

(6) Breyer, Frank G., United States Patent 1,985,076  
Dec. 18, 1934.

(7) Pontoppidan, Carl, British Patent 283,091, Jan. 5,  
1928.

(8) Breyer, Frank G., op. cit.

conflicting opinions.

Joseph Freeman Goddard and Super Cement Limited, a British Company, have obtained a patent on a process for the dry grinding of materials in which there is mixed with the material being ground a grinding aid which generates static electricity in the particles being ground causing mutual dispersion<sup>(9)</sup>. It is noticed that this process is different from that of Pontoppidan's<sup>(10)</sup> in which a difference of polarity or electrical potential was made to exist between the grinding surfaces and the fine particles.

Edward W. Scripture, Jr.<sup>(11)</sup> has obtained a patent on a claim to reduce grinding time of cement clinker by the addition of 0.05-0.1 % of salicylates, derivatives thereof and compounds containing the salicylate group, or substituted benzoic acid and its derivatives.

At the same time Scripture obtained another patent<sup>(12)</sup> on the incorporation with the clinker of 0.001-0.01 % of

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(9) Goddard, Joseph Freeman, British Patent 350,538

June 12, 1931.

(10) Pontoppidan, Carl, United States Patent 1,904,523

April 18, 1933.

(11) Scripture, Edward W., Jr., Canada Patent 421,285

July 4, 1944.

(12) Scripture, Edward W., Jr., Canada Patent 421,286

July 4, 1944.



a fatty alcohol alkali metal sulfate and a small quantity of a substituted benzoic acid.

Bond and Agthe have described the ball coating as a selective mechanical process<sup>(13)</sup>. In this process the coatings are initiated by the depositing of the finest material in scratches and pits. Larger particles become embedded therein. The initial coatings are of particles below 5 microns in diameter, while the outer coatings may be composed of particles with a diameter as large as 20 microns. In all cases coatings consist of the smallest particles in the charge.

Hill<sup>(14)</sup> has considered a change in the surface properties of material as it is ground; it is this change which causes the clinging and agglomeration. Therefore certain grinding aids are effective because they form a thin film on the surface of the particles being ground.

From the above considerations it is seen that several theories have been proposed for the flocculation

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(13) Bond, F. C. & Agthe, F. T., Am. Inst. Mining Met. Engrs., Tech. Pub. No. 1160, p. 10 (1940).

(14) Hill, Eugene Farrell, Thesis, Missouri School of Mines and Metallurgy, Rolla, Missouri, pp. 55-58, 1940.

of the fine particles and the coating of the grinding bodies. It is also seen that in some cases these theories do not seem to agree even though experiments using each theory have given positive results. From this it appears that no single theory can account for all the effects of grinding aids. Instead of a single theory perhaps it would be better to use a combination of all of them thus incorporating several grinding aids into a mixture of one.

## OBJECTIVE

Claims have been advanced for the reduction of grinding time due to the incorporation of addition agents. Theories have been proposed to account for the effect of the grinding aids. Specific objects of this research include the investigation of the comparative effectiveness of different agents and the relative effectiveness of the same agent at different fineness levels.

The effectiveness of the different agents is judged by comparing the surface area of a given weight of the ground clinker to the surface area resulting when no grinding aid was used. Conditions other than the grinding aid are held constant for the various runs.

## EXPERIMENTAL PROCEDURE

The experimental portion of this work consisted of three parts:

1. The grinding of the stock clinker.
2. The seive analysis of the ground cement particles.
3. The determination of the particle size distribution of the -200 mesh particles.

### The Grinding of the Stock Clinker

With the hope of making some comparisons between this work and the work of Hill<sup>(15)</sup>, this part of the procedure was carried out in the same way.

"The grinding of the clinker was carried out in a steel ball mill 12 inches in diameter and six inches long. The mill was lined with seven semicircular liners, equally spaced, of one and one-half inch radius.

The ball charge consisted of iron balls: 5 pounds of one inch balls, 5 pounds of 3/4 inch balls, and 5 pounds of 5/8 inch balls. The mill was driven by an electric motor, and the average mill speed was

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(15) Hill, E. F., Thesis, Missouri School of Mines and Metallurgy, Rolla, Mo., 1940.

51.5 revolutions per minute.

The clinker charge consisted of 1000 grams or 2.16 pounds of clinker. This is a weight ratio of balls to charge of 6.95 to 1.

The ball and clinker charge used, as well as the mill speed, had already been established as the conditions for greatest efficiency for this particular mill.

It has been found that a weight ratio of 6 to 1 of balls to charge most nearly meets commercial conditions, but this ratio was modified as noted above to get greater efficiency from the mill."(16)

The cement clinker which was obtained from the Missouri Portland Cement Company, St. Louis, Missouri, was first screened to separate the larger than 4 mesh from the smaller particles. The plus 4 mesh was then crushed so that it all passed a 4 mesh screen and the two portions were thoroughly mixed to obtain the stock clinker. The 1000 gram sample for each run was taken from this stock clinker. A screen analysis of the stock clinker is given in Table I, page 13.

After the grinding aid was added to the 1000 gram sample of stock clinker, it was ground for 3100

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(16) Ibid.

TABLE I:--SCREEN ANALYSIS OF THE STOCK CLINKER

Tyler Screen Mesh Number	Screen Opening Microns	% Above	% Below
4	4760	00.0	100.0
6	3360	24.2	75.8
12	1410	77.8	22.2
20	840	89.5	10.5
32	500	94.0	6.0
42	350	95.6	4.0
65	210	97.3	2.7
100	149	98.0	2.0
150	105	98.5	1.5
200	74	98.9	1.1

Specific Surface is 19 cm.<sup>2</sup> per gram

revolutions of the ball mill. Several runs were made without a grinding aid for control purposes. In all runs every thing except the grinding aid was held constant. Table II, page 15, gives a list of the grinding aids used in this work along with their chemical and physical natures and the form in which they were used.

The D. P. Acid Mix is a product of Emery Industries, Inc., Cincinnati, Ohio. Due to its very viscous and "glue like" nature it was necessary to dissolve it in a suitable solvent before adding it to the clinker.

In all cases where the grinding aid was dissolved in a solvent (benzene was used as the solvent), the solvent was completely evaporated before grinding so as to make sure that the liquid state was not influencing the efficiency of the grinding aid.

The ball mill was operated at ordinary room temperatures.

#### Seive Analysis of the Ground Cement Particles

After each batch had been ground for 3100 revolutions of the ball mill, it was removed and the ground particles was thoroughly mixed. A fifty gram sample was removed by the coning and quartering(17) method

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(17) W. S. Tyler Company, Catalogue 53, p. 19, 1940.

TABLE II:--GRINDING AIDS USED IN THIS RESEARCH

<u>Name of Grinding Aid</u>	<u>Chemical Nature</u>	<u>Physical State At Room Temp.</u>	<u>Form Used</u>
Sodium Lauryl Sulfate	$\text{NaC}_{12}\text{H}_{25}\text{SO}_4$	Solid	Dry Powder
Palmitic Acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	Melting Pt. 64°F.	Mixed with 50cc $\text{C}_6\text{H}_6$ (liquid was evaporated before grinding)
D. P. Acid Mix.	Petroleum Sulphonic Acids	Very Viscous	Mixed with 100cc $\text{C}_6\text{H}_6$ (liquid was evaporated before grinding)
Benzoic Acid	$\text{C}_6\text{H}_5\text{COOH}$	Solid	Dry Powder



and seived on a Rotap machine for 15 minutes. At the beginning of this research it was decided to remove the material from the pan at the end of the 15 minute period and seive the remaining material for another 5 minute period. It soon became evident that this was not necessary, for a good separation had been attained at the end of the initial 15 minute period.

Tyler screens of the following sizes were used at the beginning of the research: 6, 12, 20, 32, 42, 65, 100, 150, and 200 mesh. After the screening the material on each screen was weighed and the -200 mesh material saved for further size determination. After examining the results of a few complete screen analysis and noticing the constant percentages obtained on the larger screen sizes, it was decided that this was due to "dead" spaces in the ball mill and all except the 150 and 200 mesh screens were discarded.

Determination of the Particle Size Distribution  
of the -200 Mesh Particles

The Palo-Travis<sup>(18)</sup> particle size apparatus shown in Illustration I, page 17, was used for the

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(18) Travis, P. M., ASTM Bull. No. 102, pp. 29-32, 1940.



- A. Upper chamber.
- B. Joint for detaching graduated cylinder.
- C. Graduated cylinder for measuring sediment level.

ILLUSTRATION I:--APPARATUS FOR MEASUREMENT OF -200  
MESH PARTICLE-SIZE DISTRIBUTION

determinations of the size distribution of the -200 mesh particles. This apparatus was set up in a well lighted location, free from vibration, sudden changes in temperature, and drafts.

#### Selection of Liquid

In the selection of the liquid settling medium three factors, solubility, specific gravity, and specific viscosity were considered.

1. The liquid could not have any solvent or chemical action on the solid.
2. Since the difference in density of solid and liquid determine the rate of fall of the particle, the length of the test was controlled to some extent by the selection of the liquid.
3. Since viscosity of the liquid also controls the rate of fall, it also had to be considered in the selection.

After a few trials and a consideration of the above factors, it was decided to use kerosene as the liquid.

#### Selection of Dispersing Agent

A dispersing agent had to be added to get the kerosene to wet the solid cement particles. The selection of

a suitable dispersing agent was largely a matter of trial and error. The Palo-Myers general use wetting agent which was supplied with the apparatus was found unsatisfactory. About 0.5 % by volume of oleic acid was selected as being suitable.

#### Determination of Specific Gravity of Solid

The specific gravity of the -200 mesh particles was determined by measuring the increase in volume obtained by adding a weighed sample to the kerosene containing the oleic acid. In this way the weight per unit volume was found to be 3.15 grams per cc.

#### Determination of Specific Viscosity of Liquid

The time required for a volumetric pipette filled to the mark with the kerosene and oleic acid mixture to drain completely divided by the time required for the same pipette to drain of distilled water is the specific viscosity, N.

$$\text{specific viscosity (N)} = \frac{\text{time for liquid}}{\text{time for water}}$$

The value of N was found to be 1.12.

#### Determination of Specific Gravity of Liquid

The specific gravity of the kerosene containing the

oleic acid was determined by means of a Westphal balance to be 0.804.

### Particle Size--Time Relation Chart

The particle size--time relation was determined by means of the conventional Stokes law formula,

$$D = 2000 \sqrt{\frac{9Nh}{2g t (d_1 - d_2)}}$$

where, D is particle diameter (microns)  
 N is specific viscosity liquid  
 h is height of fall (cm)  
 g is acceleration of gravity = 980  
 t is time of fall (seconds)  
 d<sub>1</sub> is specific gravity of solid  
 d<sub>2</sub> is specific gravity of liquid

Solving the above for t it is found that,

$$t = \frac{18,000,000 N h}{g (d_1 - d_2) D^2}$$

Since all the quantities except t and D are constant throughout each test, the equation may be reduced to,

$$t = \frac{k}{D^2} \quad \text{where,} \quad k = \frac{18,000,000 N h}{g (d_1 - d_2)}$$

Table III, page 22, shows the various particle sizes on which data were desired and the time of fall computed for each using the formula,  $t = k/D^2$ . Column IV is the sediment level recorded at the calculated times. Column V is column IV divided by the total sediment and multiplied by 100. Column VI is 100% minus column V. An interpretation of line 3 would be that 10.4 % of the sample is above 50 microns in diameter while 89.6 % of the sample is below 50 microns in diameter.

TABLE III:--PARTICLE SIZE--TIME RELATION CHART

I	II	III			IV	V	VI
D Microns	TIME Sec.	TIME H M S			SED.LEV. mm	% ABOVE	% BELOW
74	000	0	0	00	0.0	0.0	100.0
60	260	0	4	20	1.0	4.3	95.7
50	370	0	6	10	2.4	10.4	89.6
40	580	0	9	40	4.6	19.9	80.1
35	760	0	12	40	6.0	26.0	74.0
30	1040	0	17	20	7.8	33.8	66.2
25	1500	0	25	00	9.8	42.4	57.6
20	2300	0	38	20	12.3	53.3	46.7
15	4200	1	10	00	16.7	72.4	27.6
12	6600	1	50	00	21.0	91.0	9.0
10	9500	2	38	20	23.0	99.6	0.4
Sediment level when liquid had cleared--23.1							

### Procedure for Particle Size Distribution

Following is the consecutive steps of each determination.

1. The settling tube was filled to slightly above the stopcock with a portion of the previously prepared stock solution of the liquid medium, kerosene and oleic acid.
2. The stopcock was closed.
3. A representative sample of 4.5 grams of the -200 mesh cement to be tested was added in the dry state to the upper chamber of the settling tube.
4. The dry cement was intimately mixed with the liquid in the upper chamber.
5. The stopcock was completely opened and at the same time the electric clock timer was started.
6. The height of the sediment in the collecting tube was recorded at the previously determined times as recorded in Table III, page 22. If the sediment was not level in the collecting tube, it was leveled before each reading by tapping the tube with a pencil.
7. The test was allowed to proceed until the liquid had cleared, or until a time interval



of one hour showed no appreciable rise in the sediment level.

8. The total sediment level was recorded.

The room temperature was kept between 24° C. and 26° C. on all determinations.

## DATA AND CALCULATIONS

### Seive Analysis of the Ground Clinker

The author was able to check Hill's<sup>(19)</sup> observation that the seive analysis of the plus 150 mesh material was essentially the same for all the samples, and only varied in the amounts on the 200 mesh screen and the amount passing the 200 mesh screen. No conclusions from this observation was made by Hill.

Throughout this research it was believed that the above observation was possible due to the fact that the nature of the construction of the mill provided several "dead" spaces. After a particle became lodged in one of these spaces, it was not touched by the balls. For this reason it was believed that data on the plus 200 mesh particles were valueless in analyzing the effectiveness of the grinding aids. However it was recognized that there was a variation in the percentages of the different samples passing the 200 mesh screen. A plot showing these variations is presented in Figure 1, page 26. From this plot it is clearly seen that there is an increase of from about 1 % to about 7 % in the amount

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(19) Hill, E. F., op. cit., p. 19.

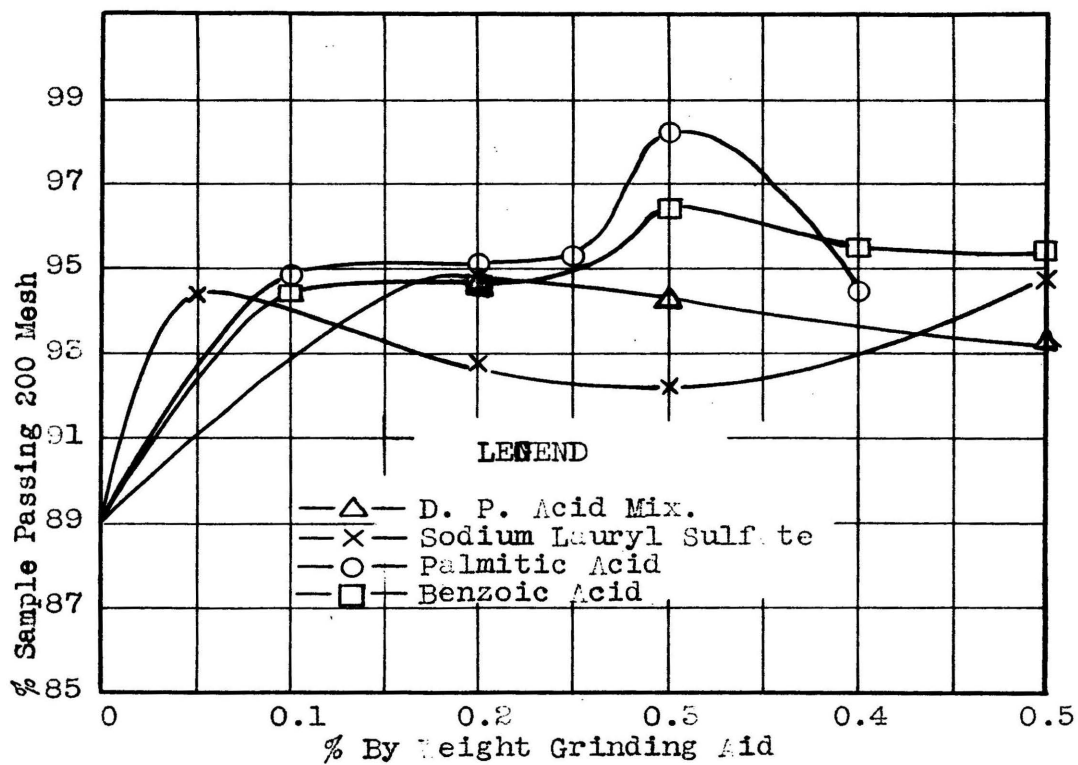


FIGURE 1:--THE EFFECT OF GRINDING AIDS ON THE AMOUNT OF SAMPLE PASSING 200 MESH.

of sample passing the 200 mesh screen when a grinding aid was used over the amount passing when no grinding aid was used. In each case there seems to be an optimum amount of grinding aid to be added to obtain a maximum percentage passing the 200 mesh screen. However this optimum is not necessarily the same as the one for obtaining maximum specific surface.

Determination of the Specific Surface of  
the -200 Mesh Material

It can be shown that the specific surface of the fraction of a material between two different particle diameters can be given by the expression,  $f = k/\rho D_{av}$ . where,  $f$  = the specific surface in  $\text{cm.}^2/\text{gm.}$  of the fraction of the sample whose average particle diameter is  $D_{av}$ .

$\rho$  = the density of the material in  $\text{gm./cc.}$

$D_{av}$ . = the average particle diameter in  $\text{cm.}$  of the given fraction.

If the particles are assumed to be spherical,  $k = 6$ .(20)

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(20) Walker, Lewis, McAdams, and Gilliland, Principles of Chemical Engineering, 3rd ed., N. Y., McGraw Hill, 1937, p.253.

Then the partial specific surfaces are given by the equation:

$$\Delta A = \frac{\Delta S f}{100}$$

where,

$\Delta A$  = the portion of the specific surface in cm.<sup>2</sup>/gm. of the entire sample contributed by the fraction corresponding to the percentage  $\Delta S$ .

$\Delta S$  = the percentage of the sample whose particle diameter is  $D_{av}$ .

Then the summation of all the  $\Delta A$  values will be the specific surface of the entire sample. The material below 10 microns in diameter was assumed to have an average diameter of 5 microns.

The term,  $\Delta D$ , is used to indicate the particle size range taken for a given fraction. Then the term,  $\Delta S/\Delta D$ , represents per cent per micron. Table IV, page 29, shows a complete set of calculated data on a representative run.

TABLE IV:--CALCULATION OF THE SPECIFIC SURFACE OF THE  
-200 MESH MATERIAL

D Microns	TIME Sec.	SED.LEV. mm	% ABOVE	% BELOW	$\Delta S$ %	$\Delta D$	$\frac{\Delta S}{\Delta D}$	r	$\Delta A$
74	000	0.0	0.0	100.0	---	00	----	---	--
60	260	1.0	4.3	95.7	4.3	14	0.31	284	12
50	370	2.4	10.4	89.6	6.1	10	0.61	347	21
40	580	4.6	19.9	80.1	9.5	10	0.95	424	40
35	760	6.0	26.0	74.0	6.1	5	1.22	508	31
30	1040	7.8	33.8	66.2	7.8	5	1.56	587	46
25	1500	9.8	42.4	57.6	8.6	5	1.72	693	60
20	2300	12.3	53.3	46.7	10.9	5	2.18	847	92
15	4200	16.7	72.4	27.6	19.1	5	3.82	1090	208
12	6600	21.0	91.0	9.0	18.6	3	6.20	1413	263
10	9500	23.0	99.6	0.4	8.6	2	4.30	1735	149

Total sediment level  
when liquid had  
cleared 23.1 mm.

0.4    10    0.04    3810    15  
Cm.<sup>2</sup>  
Specific Surface    ----- = 937  
Gm.

Comparison of Particle Size Measurements Made  
With Palo-Travis Apparatus to Those Determined  
by the Wagner Turbidimeter

Since it was believed that the specific surfaces as calculated by the use of the Palo-Travis apparatus were lower than reports by other methods, it was desired to check this method against one which had been used more for cement. The Wagner turbidimeter method<sup>(21)(22)</sup> was selected. A sample which had been found to have a specific surface of 1760 cm.<sup>2</sup>/gm. by the Wagner turbidimeter method was obtained from the Missouri Portland Cement Company, St. Louis, Missouri. Four runs by the Palo-Travis method were made upon this sample and specific surfaces of 933, 919, 921, and 891 cm.<sup>2</sup>/gm. were obtained. With 916 as an average this was a maximum deviation of 2.73 %. This might be compared with the maximum of  $\pm 3.0$  % which is the deviation on the Wagner turbidimeter method.

Although it is possible to get good check results with the Palo-Travis apparatus, the results in this case were  $(916/1760) \times 100 = 52$  % of the accepted results.

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(21) Wagner, L. W., A. S. T. M. Proc. 33 (II), 533, 1933.

(22) A. S. T. M. Tentative Standards, C 115-34T, 1935.

Since all the analysis of data for grinding aids is done on a comparative basis, this failure of the two methods to check will not lessen the value of these experiments.



## INTERPRETATION OF DATA

### Optimum Amount of Grinding Aid for Maximum Specific Surface

By means of the method described on page 27, the specific surface of all the samples were calculated. Figure 2, page 33, shows these values plotted against the percent by weight of addition agent with each of the curves starting from a point representing the surface area when no addition agent was added. It is seen that the specific surface increases when a grinding aid is added, thus giving a definite and clear picture of the overall effect of grinding aids. The curves rise at varying slopes for the different grinding aids until a maximum peak is reached. Then they either level off or show a decrease in specific surface. This peak represents the optimum amount of grinding aid for a maximum specific surface.

The sodium lauryl sulfate gives a peak surface area at about 0.1 per cent. The peaks with palmitic acid and D. P. Acid Mix. are given by 0.3 and 0.4 % addition agent respectively. The benzoic acid gives a gently rising curve leveling off at 0.4 to 0.5 % of grinding aid.

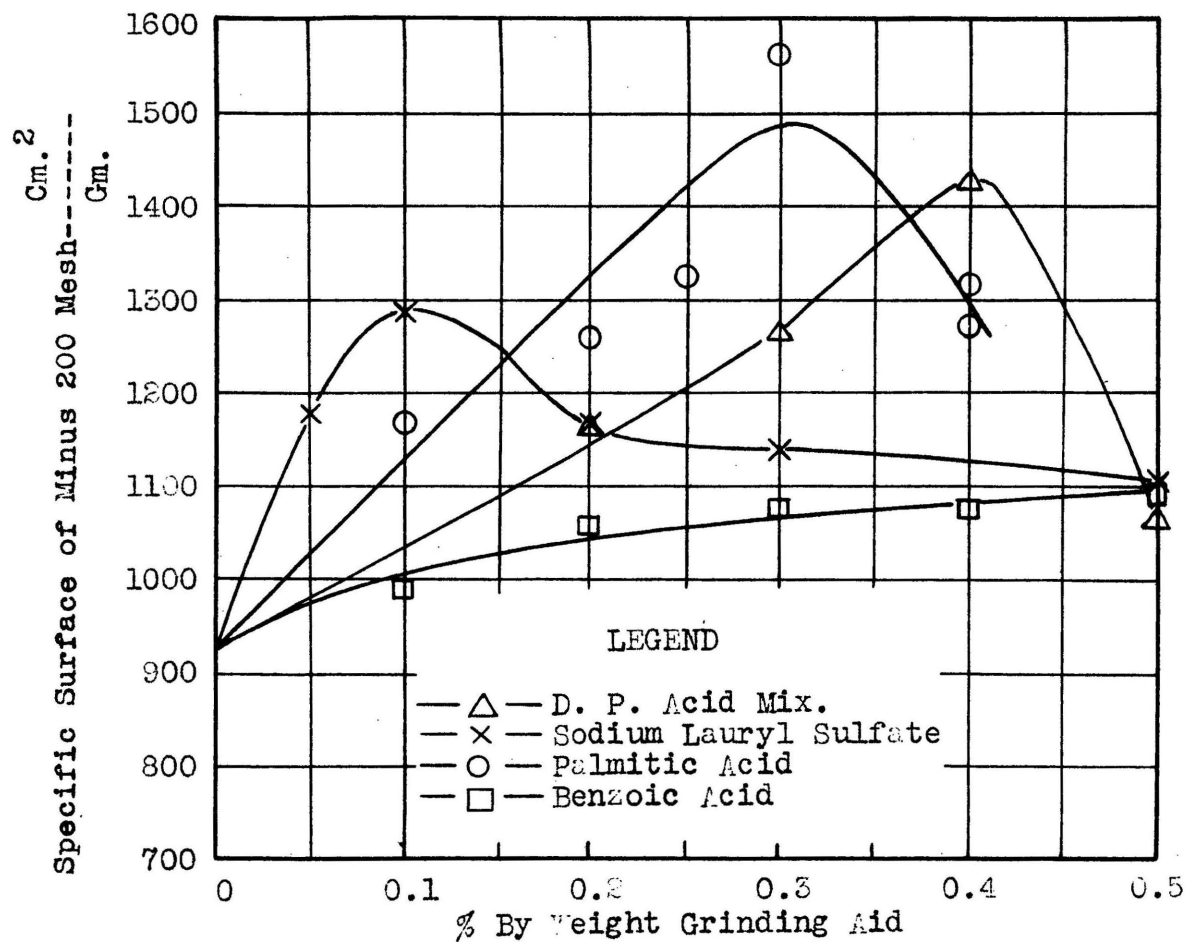


FIGURE 2:--SPECIFIC SURFACE OF CEMENTS USING VARIOUS GRINDING AIDS.

A favorable comparison can be made between the peaks for D. P. Acid Mix. obtained in this work and in the work of Hill.<sup>(23)</sup> Hill's peak occurred at 0.35 % by weight grinding aid compared with a value of 0.4 % here.

Comparison of Various Grinding Aids

Basing the conclusion only upon the surface area obtained with the use of the various grinding aids, it appears that palmitic acid is the best addition agent with D. P. Acid Mix., sodium lauryl sulfate, and benzoic acid following in the order of decreasing value. Of course it is realized that there are many other things such as cost, availability, ease of introduction, and effect upon the final concrete product which would influence the selection of a grinding aid. These latter factors were not considered in this research.

Also as will be shown in another section the specific surface of a sample does not have any direct relation to the percentage distribution of particles with a definite diameter.

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(23) Hill, E. F., op. cit., p. 47.

Relative Effectiveness of Grinding Aids at Different Fineness Levels.

In order to show the particle size distribution of the -200 mesh material and to determine the relative effectiveness of the various addition agents at different fineness levels, a plot of per cent per micron ( $\Delta S/\Delta D$ ) versus particle diameter (microns) was made. As about twenty graphs would be necessary to show a complete picture of these results for the various grinding aids, only one representative plot comparing a sample ground with no grinding aid to a sample ground with 0.1 % sodium lauryl sulfate is presented. The same general type of plot would be obtained for the other samples. Figure 3, page 36, shows the representative plot. This plot illustrates the effect of grinding aids upon the particle size distribution. This type of plot when plotted for all the samples could be used for obtaining the optimum per cent of the best grinding aid for obtaining a product containing a maximum of a given particle size. It is noticed on this plot that the amount of fines below 10 microns increases 300 % when the grinding aid is added. However for the plus 10 micron size particles the percentage per micron is greater when no grinding aid is added.

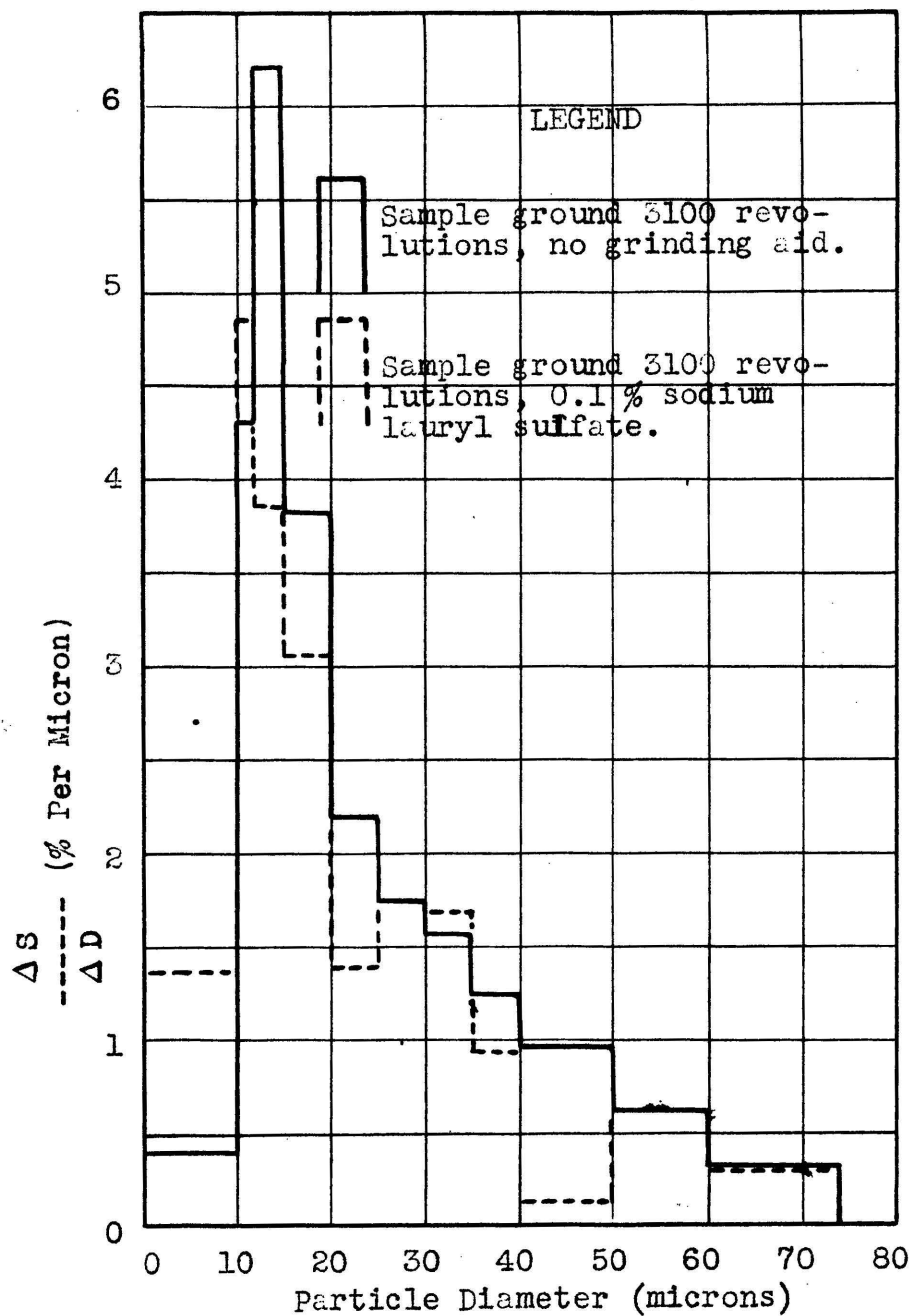


FIGURE 3:--PARTICLE SIZE DISTRIBUTION OF  
-200 MESH MATERIAL.

The same general results might be obtained from the series of Figure 4 curves. However in this type of plot where the per cent of particles between two diameters is plotted versus the per cent by weight of addition agent it is a little more difficult to select the diameters between which the largest percentage distribution of the sample is found. The type of curve shown in Figure 4 has the advantage over the curve of Figure 5 in that it allows more samples to be compared on the same plot.

Both types of curves show that the amount of addition agent to be used should be governed by the particle size range desired in the product.

It is realized that specifications for a cement might call for a given percentage of the cement particles to be finer than a certain diameter. In such a case the series of Figure 5 curves in which the per cent of particles finer than a given diameter is plotted versus per cent by weight of addition agent would be the type to use for the selection of the addition agent and the optimum amount of it to be used.

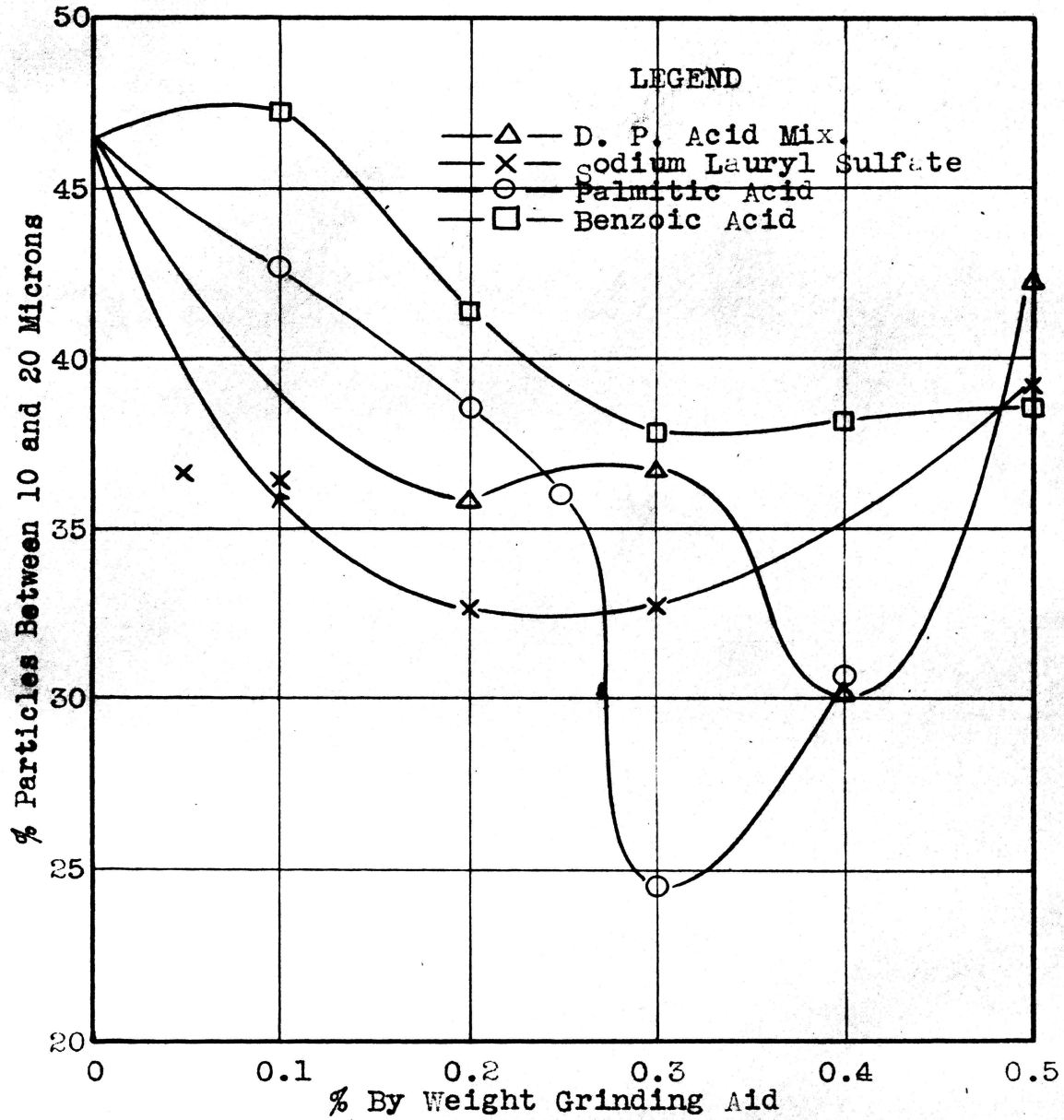


FIGURE 4a:--COMPARISON OF THE EFFECTIVENESS OF GRINDING AIDS AT SPECIFIC FINENESS LEVELS.

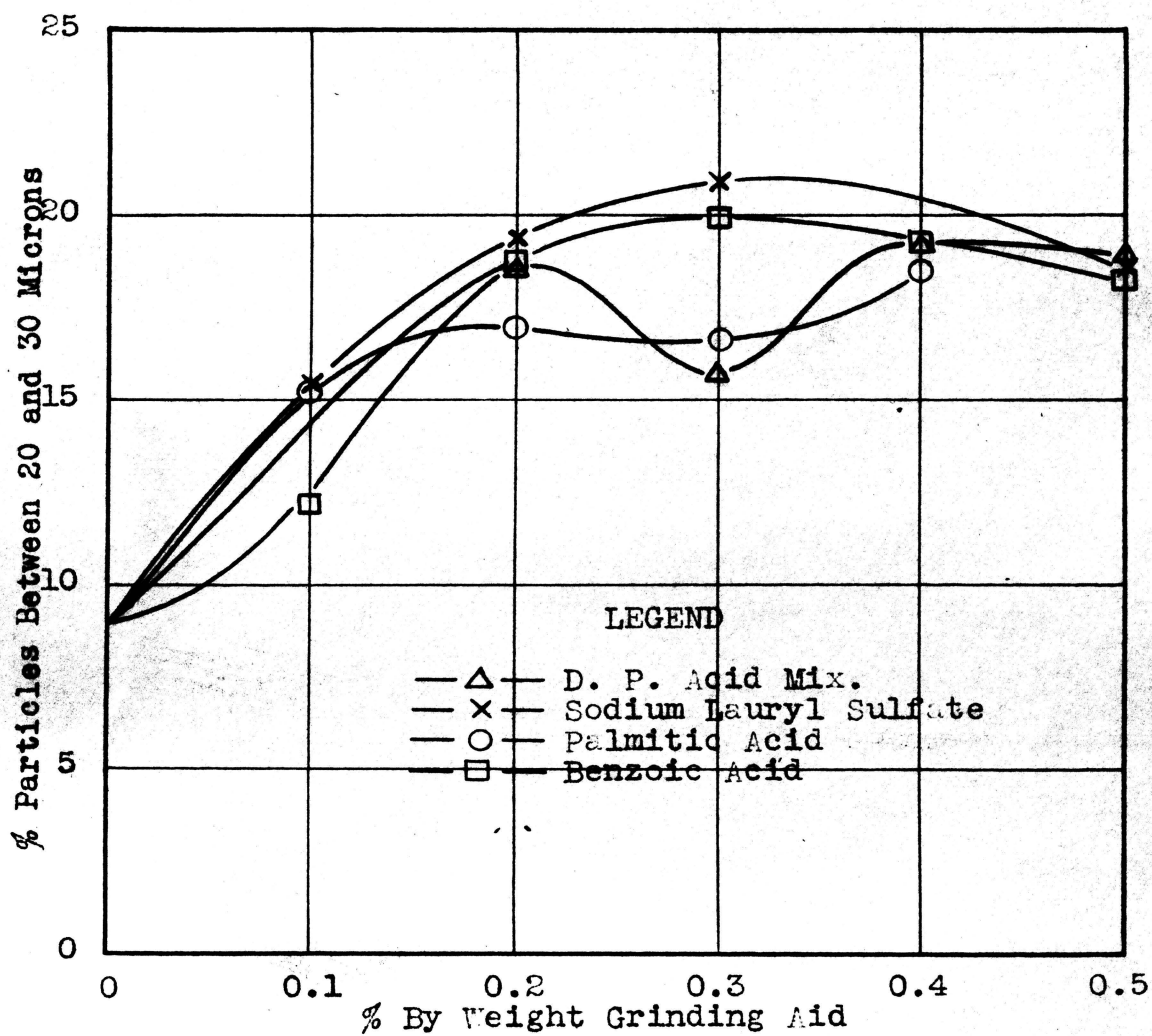


FIGURE 4b:--COMPARISON OF THE EFFECTIVENESS OF GRINDING AIDS AT SPECIFIC FINENESS LEVELS.



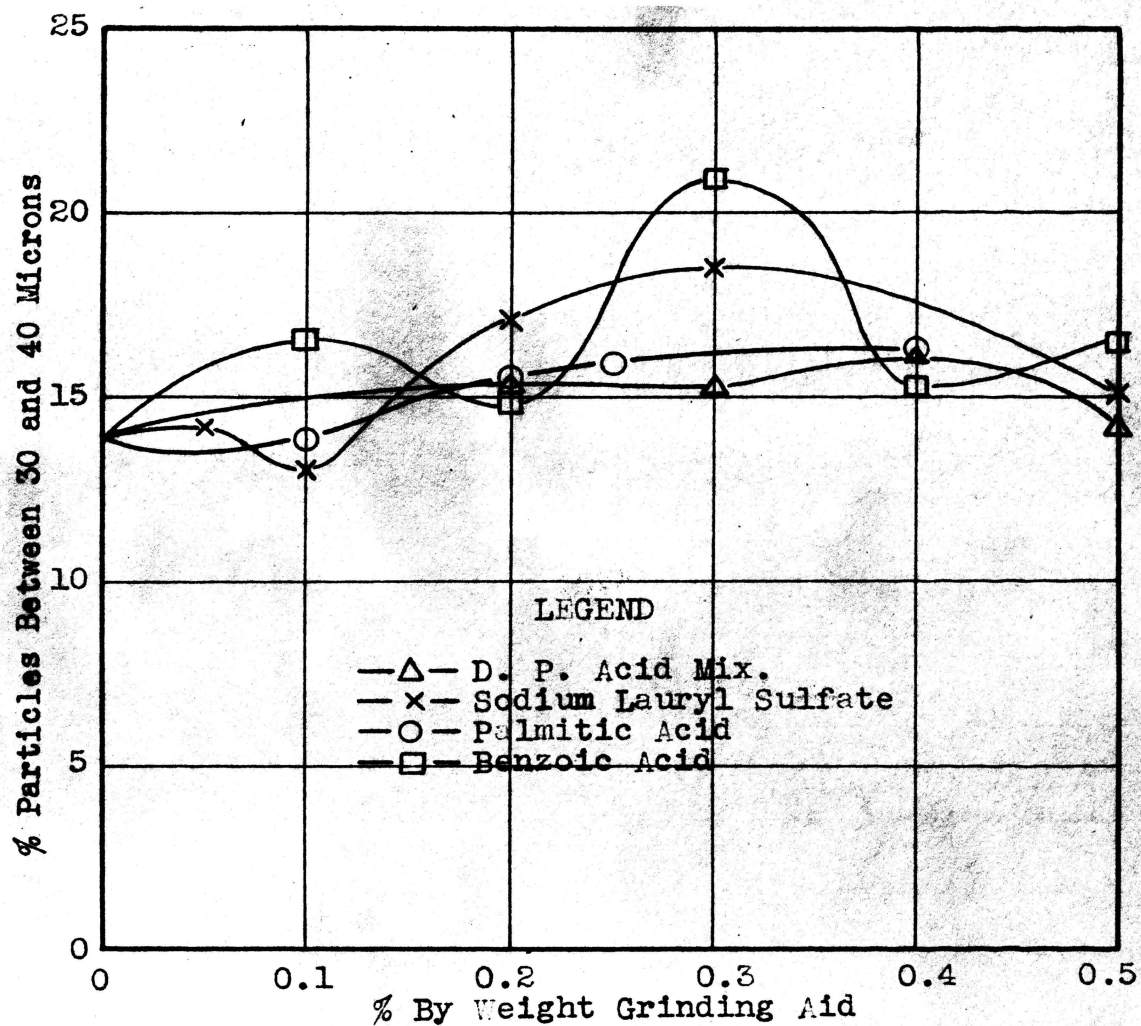


FIGURE 4c:--COMPARISON OF THE EFFECTIVENESS OF GRINDING AIDS AT SPECIFIC FINENESS LEVELS.

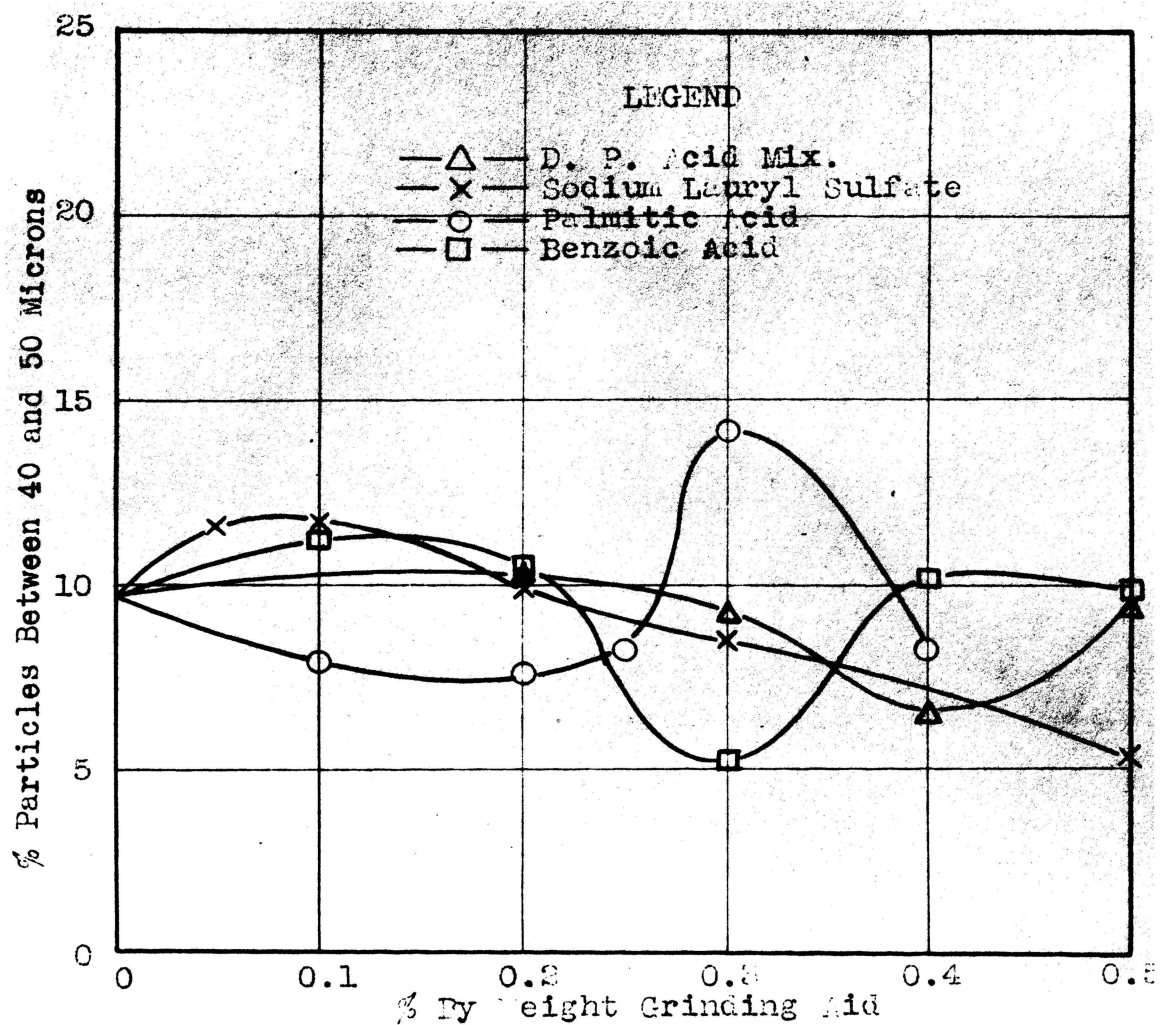
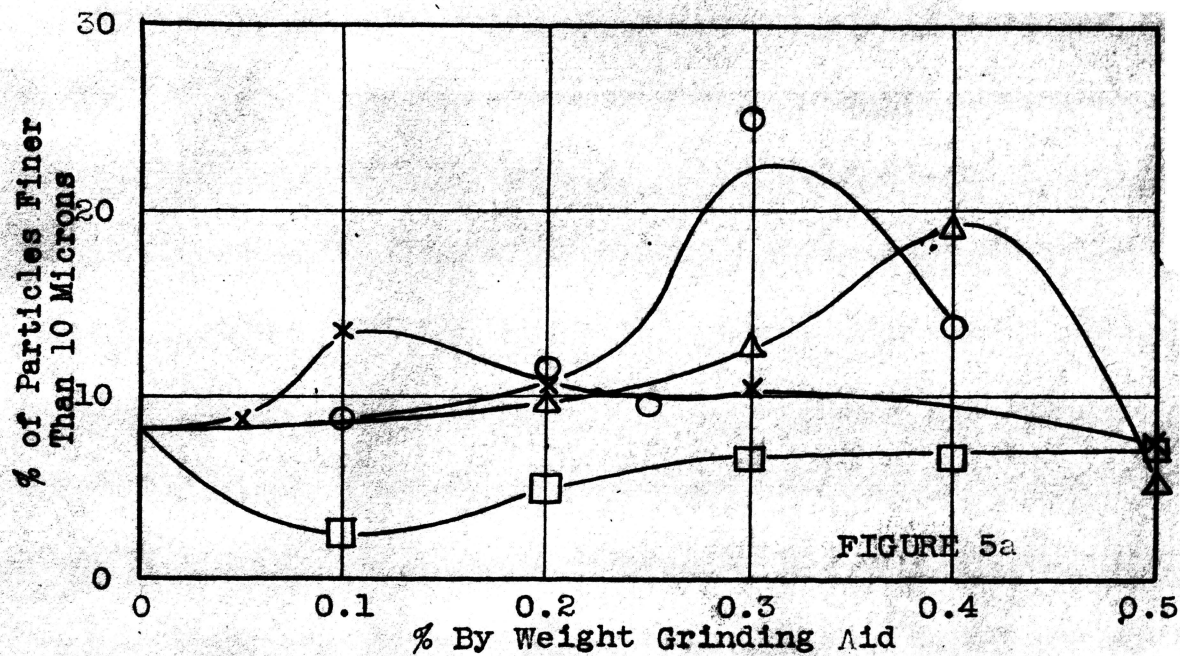


FIGURE 4d:--COMPARISON OF THE EFFECTIVENESS OF GRINDING AIDS AT SPECIFIC FINENESS LEVELS.



LEGEND

- △— D. P. Acid Mix.
- ×— Sodium Lauryl Sulfate
- Palmitic Acid
- Benzoic Acid

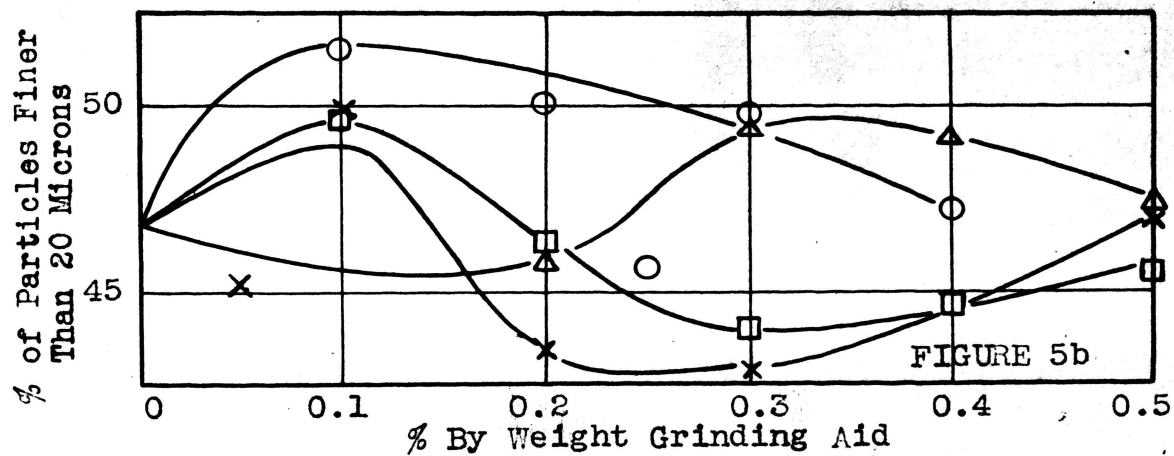
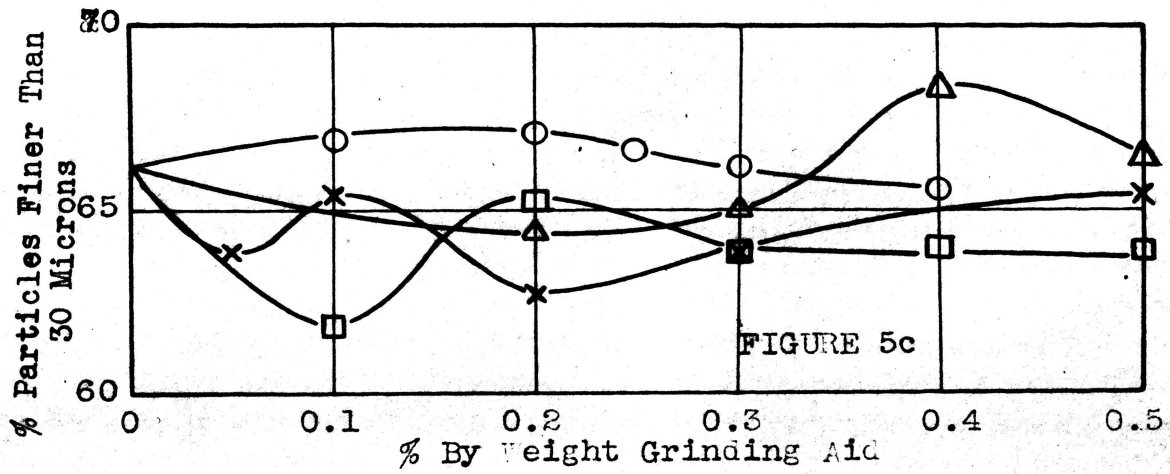


FIGURE 5a, 5b;--COMPARISON OF THE EFFECTIVENESS OF GRINDING AIDS AT DIFFERENT FINENESS LEVELS.



LEGEND

- △— D. P. Acid Mix.
- x— Sodium Lauryl Sulfate
- Palmitic Acid
- Benzoic Acid

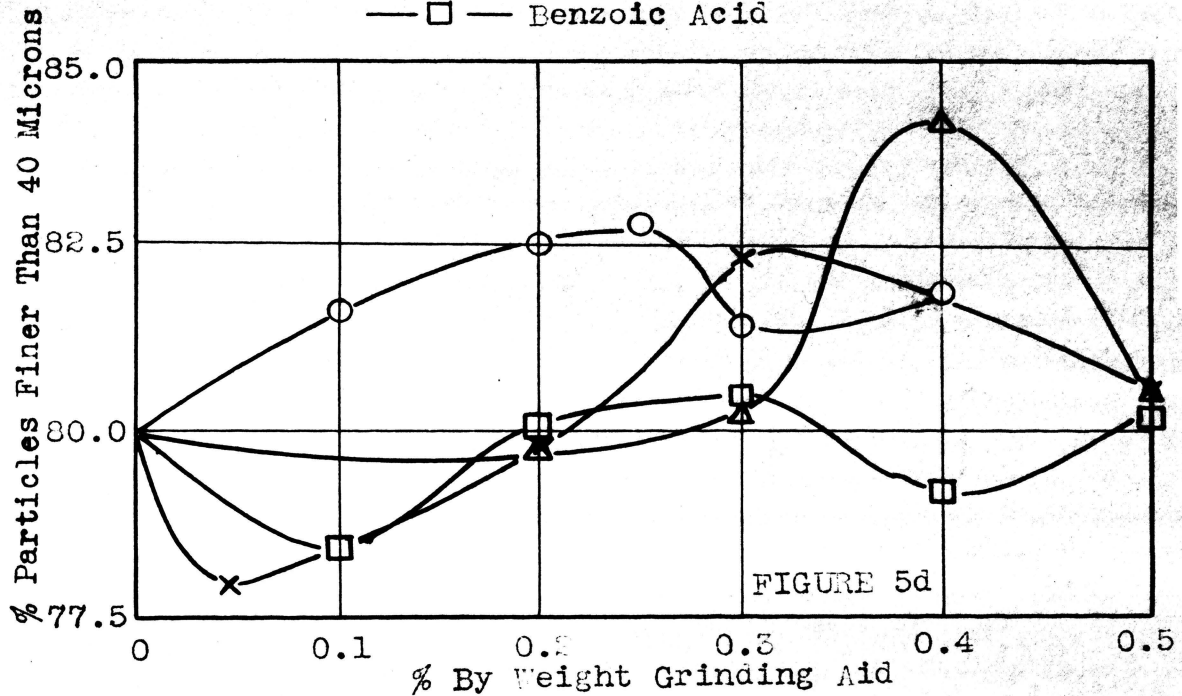
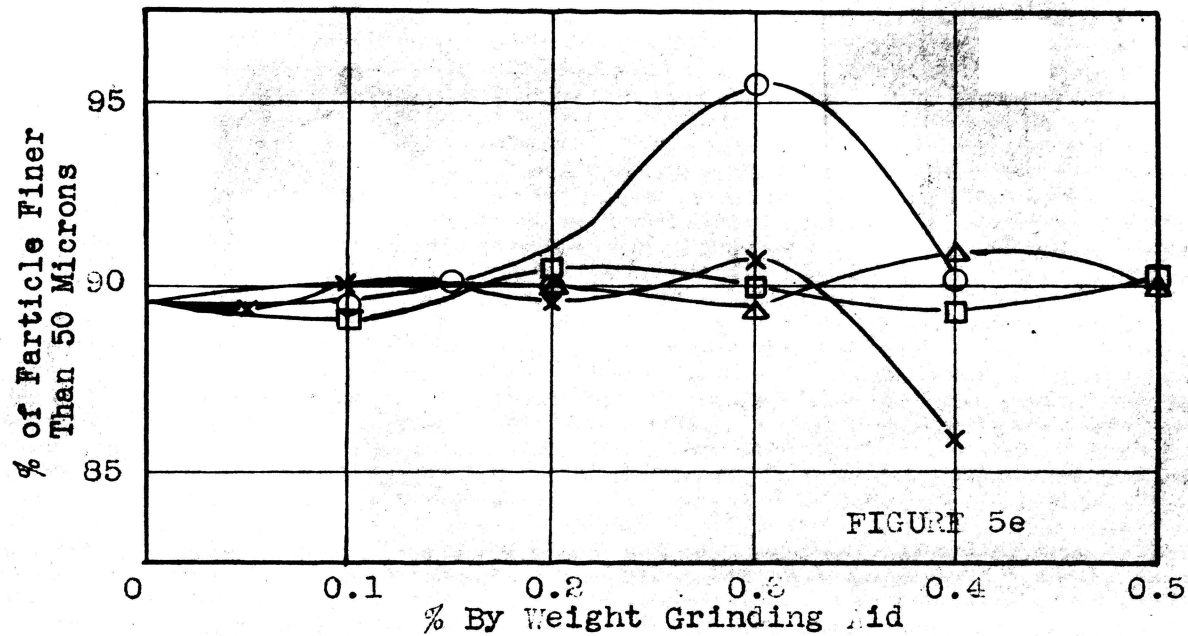


FIGURE 5c, 5d:--COMPARISON OF THE EFFECTIVENESS OF GRINDING AIDS AT DIFFERENT FINENESS LEVELS.



LEGEND

- △— D. P. Acid Mix.
- x— Sodium Lauryl Sulfate
- Palmitic Acid
- Benzoic Acid

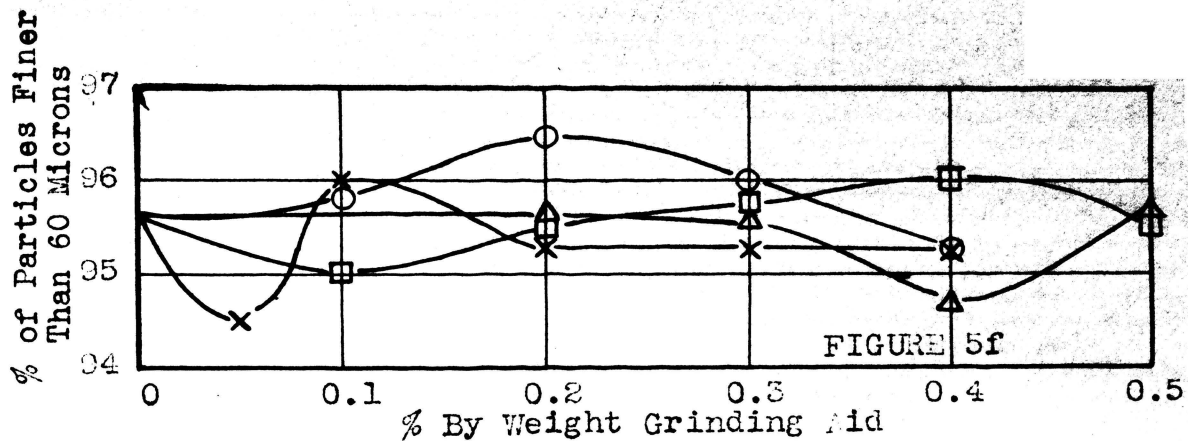


FIGURE 5e, 5f:--COMPARISON OF THE EFFECTIVENESS OF GRINDING AIDS AT DIFFERENT FINENESS LEVELS.

### Effect of Solvent As a Grinding Aid

The solvent, benzene, was added to the D. P. Acid Mix. and to the palmitic acid in order to increase its chances of spreading over the entire sample of cement clinker. Before the grinding was performed, the solvent was completely evaporated so that the liquid would not affect the grind. However it was thought that there might be enough of the benzene left on the dry sample or that some chemical change might have taken place so as to affect the results of these runs.

When 50 cc of benzene only (no addition agent) was added to the clinker and evaporated before grinding the resulting specific surface was  $1246 \text{ cm.}^2/\text{gm.}$ , which is a larger value than was obtained by use of some of the dry (no solvent) addition agents. In this case it was noticed that there was quite a coating on the balls and mill at the end of the grinding period. For this reason along with the increase of surface area over the  $937 \text{ cm.}^2/\text{gm.}$  obtained when nothing was added, it might be thought that in addition to the theories given by other writers that there is a factor other than the cushioning of the blows of the balls which tends to decrease the efficiency of grinding.

In any event it is noticed that the solvent has a large effect upon the surface area obtained. The low specific surfaces obtained when benzoic acid and sodium lauryl sulfate were added as a dry powder might be attributed to the fact that the dry powder has less covering power than a liquid mixture.



### SUMMARY

1. The effect of various percentages of a number of grinding aids upon the surface area of ground cement clinker has been investigated.
2. An optimum amount of the grinding aid was found in each case for a maximum specific surface. When greater amounts of the grinding aid were used the surface area of the ground clinker decreased.
3. The particle size distribution of the -200 mesh material obtained by using various percentages of different grinding aids was studied. It was found that the relative effectiveness of different grinding aids varied at different fineness levels.
4. Three different methods for plotting data showing the particle size distribution have been presented.
5. The effect of grinding aid solvents has been shown to be a tremendous factor in the overall surface areas.



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